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ONR FINAL REPORT

MANY-BODY QUANTUM MECHANICAL STUDIES OF MOLECULAR CLUSTERS

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Abstract

The following final report summarizes four years of research for ONR on the topic of "Many-Body Quantum Mechanical Studies of Molecular Clusters." There are two primary aspects of this effort, a methodological part focusing on new first principle (i.e. *ab initio*) multi-reference coupled-cluster methods for obtaining improved solutions to the Schrödinger equation for the structure and spectra of molecular clusters; and applications of these new, coupled-cluster (CC) and many-body perturbation theory (MBPT) methods to several fascinating problems with emphasis on the structure and spectra of carbon clusters and borane (BH_3) containing clusters. The substantial accomplishments of this effort are summarized.

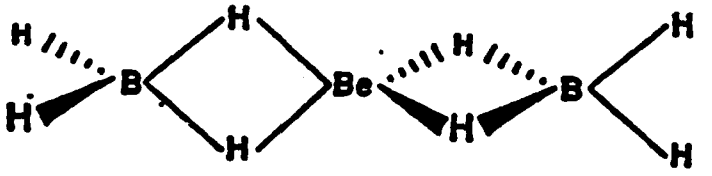
Summary of Progress

Our four-year effort for ONR on the topic of Many-Body Quantum Mechanical Studies of Molecular Clusters has paid many dividends, both in methodological advances and in applications. Although the applications and the questions they have resolved is the ultimate objective of our studies, our studies on interesting clusters have been made possible by critical methodological advances. Only with such essential advances in ways to more accurately and efficiently approximate the Schrödinger equation is it possible to reliably predict molecular structure and spectra, the relative stabilities of isomeric forms, and the transition states that lead to activation barriers to dissociation. For transient molecules, which include most clusters, many properties are only obtainable via *ab initio* quantum mechanical methods. If these results are to be predictive, to provide reliable information in the absence of experiment, or to offer a third voice to resolve experimental discrepancies, new and more accurate methods have to be continually developed. The development of such methodological tools is a primary objective of our research on clusters for ONR, complemented by the application of these novel methods to studies of a variety of cluster types. The following first summarizes some of our novel applications of new theoretical methods for clusters and then the new methodological advances we have made in the course of this project for ONR.

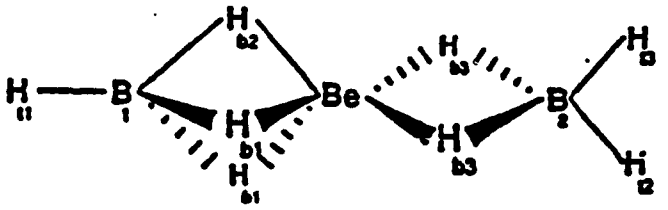
Cluster Studies

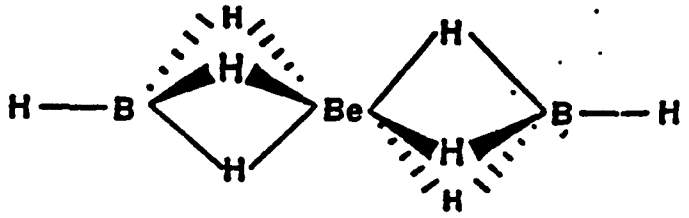
I. Boron Clusters

A. The fifty-year old problem of the unknown structure of the mixed cluster, $Be(BH_4)_2$ has been resolved [A3].* Inspite of numerous different types of experimental studies that reached at least six different, contradictory conclusions, we were able to resolve the problem by predicting from first principles the vibrational spectra of certain of the $Be(BH_4)_2$ isomers, namely

I. 

* References to publications derived from this project are indicated by an A preceding the number and refer to those in the publication list on pages 17-19. Other references are indicated just by a number and are listed on page 16.

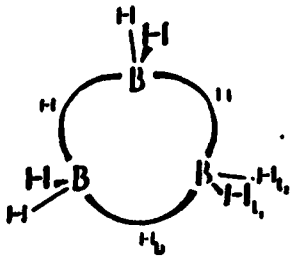
II. 

III. 

These predictions were made possible by the recent development of correlated analytical (first-derivative) gradients [1] and hessians (i.e. second derivatives) for molecular displacement [2] (see [A34] for a review). The latter, provides the harmonic force constants and, consequently, the vibrational frequencies for molecules. Additionally, the derivatives of the dipole moment provide the associated infra-red intensities [A13]. Combining the two, it is possible to simulate a molecule's spectra from first principles. Using this tool, we determined that the experimental IR spectra of Nibler consisted of the two isomers, I and III. Furthermore, upon matrix isolation, only III remained. Nibler's interpretation that the correct structure was a displaced C_{3v} structure of III, partly precipitated by independent experiments suggesting that the molecule had a dipole moment, was erroneous. Furthermore, by accurate computation, structure II was found not to be a minimum on the potential energy surface. Also, our calculations demonstrated that it could not have a dipole moment anywhere near the large 2.1 D value observed.

B. Another interesting cluster study of this type pertains to $BH_3 + H_2$. The question is whether the BH_5 molecule exists as a bound species [A20]. The extreme accuracy required to answer this question could only be achieved with large basis coupled-cluster methods. Furthermore, the potential for tunneling had to be assessed to reach conclusions about the stability of BH_5. We performed these studies and concluded that BH_5 was stable by 2 kcal/mol. We also performed an estimate of the tunneling, concluding that the molecule should have a reasonable lifetime despite tunneling.

C. A third interesting application dealt with the experimentally unknown triborane $(BH_3)_3$ cluster [A17]



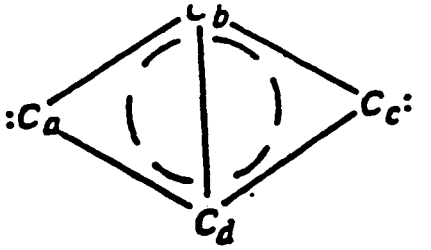
It is a proposed intermediate in the synthesis of higher boranes, and its ephemeral existence has been supported by mass spectroscopy, but there is no other substantiation of its existence. Electron correlation is critical in obtaining correct results for electron deficient systems, and we use the highly accurate coupled-cluster methods we have developed, specifically CCSD+T(CCSD), to obtain results for its structure and energetics, as well as SCF predictions of vibrational frequencies. It is found to be stable by 9.3 kcal/mol relative to $BH_3 + B_2H_6$ but thermal and entropic effects lead to a free energy change favoring the products.

II. Carbon Clusters

A. We have also made an extensive set of applications to the fascinating carbon clusters, C_n [3]. These molecules have often been proposed to be responsible for the so-called diffuse spectra in interstellar space. Forms of carbon clusters, the fullerenes, have now been found to have superconducting properties. They have also received much attention from a wealth of experimentalists like Rich Smalley and John Eyler, who are similarly supported by the ONR cluster program. This encourages an unusually profitable synergism between theory and experiment. Our first studies from 1986 [4] were precipitated by limited experimental observations of neutral C_4 in matrix isolated ESR studies by Weltner, et al. Weltner et al. [5] assigned an electronic excitation at 2.42 eV assumed to be either the $^3\sum_u^-$ or $^3\Pi_u$ state of linear C_4. Using MBPT(4) [6] we predicted the $^3\sum_u^-$ state to lie at 2.8 eV, considered to be in reasonable agreement with the observation. In addition, a forbidden excitation to the $^3\Pi_g$ state was indirectly estimated in the ESR experiment to lie at less than 0.7 eV. MBPT(4) finds the state at 0.8 eV, also in good agreement with the experimental estimate.

B. The experiment also assigned vibrational spectra, observing two lines, at 2164 cm^{-1}, assigned to C_4, and 1544 cm^{-1}, assigned to C_5 [5]. The treatment of vibrational spectra benefits enormously from the development of methods for the analytical evaluation of first derivatives of the electronic energy with respect to atomic displacement (gradients) [1,A14], and, if available, the second derivatives (hessians) [2,A15,A34]. The former facilitate the prediction of the structure of a molecule while the latter, obtained analytically or as the numerical difference of analytically computed first derivatives, provides the force constants for predictions of the vibrational spectra. Similarly, one can obtain the derivatives of the dipole moment with atomic displacement to provide the IR intensities. At the second-order MBPT level, MBPT(2) predictions of the frequencies for C_4 linear and rhombus were reported by ourselves [4,A6] and others [7]. Unlike the experimentally assigned lines, the 1544 cm^{-1} frequency belongs to C_4, not C_5, corresponding to the theoretical prediction of 1586 cm^{-1}. Furthermore, recent experiments by Bernath et al. [8] and Saykally et al. [9] definitively assign the 2164 cm^{-1} line to C_5, not C_4. The linear C_4 frequencies have been very recently observed by Graham in matrix isolation further verifying the theoretical assignment [10].

C. A conceivable alternative to the linear triplet C_4 structure is to have all electrons pair into a cyclic (rhombic) structure [4,12,A6],



The bond angles are 63° and 117° [4]. The cost, of course, is the ring strained engendered by forcing two C atoms to have a bond angle of 63° compared to the more normal tetrahedral values. This raises the question of comparative stability of the forms of C_4 and other C_{2n} species. In the course of our analysis of linear C_4's spectra, we also investigated the relative stability and spectra of the lowest energy cyclic, rhombic form. This study [A6] has led to some intriguing questions and new experimental observations. At the SCF level, the linear form is much preferred, while once correlation is introduced at even the second order level, MBPT(2), the order is reversed. At MBPT(4) the energy difference is reduced somewhat as also occurs when the (4s2p1d) basis is expanded to a (5s3p1d) basis. For very high accuracy correlated results, it is frequently necessary to go beyond the MBPT level, and include important correlating terms to all orders [13]. This is accomplished very nicely with coupled-cluster methods. Just as SDQ-MBPT(4) includes all effects of single, double and quadruple excitations through fourth-order in electron correlation, the coupled-cluster single and double excitation model, CCSD, built upon the exponential wavefunction, $exp(T_1 + T_2)|\Phi_0\rangle$, sums all such terms to infinite order. Similarly, (SDTQ)-MBPT(4) is the fourth-order approximation to CCSDT or the simpler modification CCSDT-1 that includes triple excitations [13]. CCSDT-1 results suggest that the $^1A_1$ rhombic form of C_4 and the $^3\sum_g^-$ linear form are almost isoenergetic. Their energy difference is computed to be only about 1 kcal/mol [A6]. Since these structures correspond to different electronic states with different multiplicities on a potential energy surface, in the absence of spin-orbit interactions, the two forms of C_4 cannot interconvert. Hence, we should have both species in a C_4 sample. However, thermodynamics favors the linear C_4 by about 10 to 1 [14]. Hence, any experimental observation of the predicted rhombic isomer will require an approach that can selectively isolate the lesser isomer.

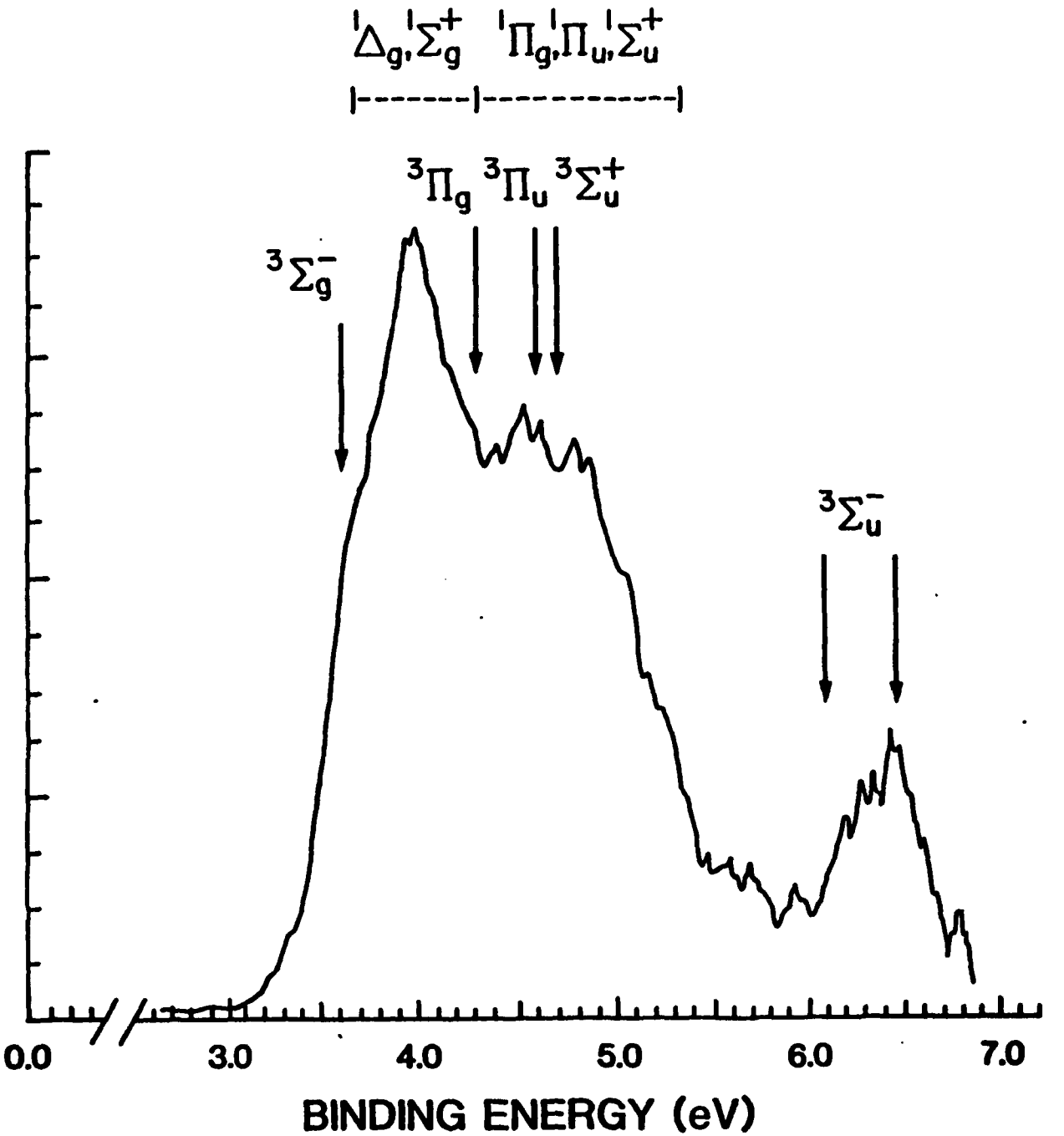
D. The next interesting experiments pertaining to C_n clusters were the photoionization experiments of Smalley, et al. [15]. By attaching an electron to form C_n^- and then photoionizing the anion, $C_n^- \rightarrow C_n + e^-$, the photoelectron spectra is obtained with peaks depending upon which e^- was removed from C_n^-. To facilitate the prediction of these spectra, we introduced another new CC theoretical method built upon a quasi-restricted Hartree Fock (QRHF) reference function [16]. We choose Φ_0 to be a QRHF function, i.e. a single determinant reference composed of the orbitals taken from the neutral cluster, occupied to ensure maximum double occupancy up to the unpaired electrons. Such a high spin reference function is a spin eigenfunction, $\hat{S}^2\Phi_0 = S(S+1)\Phi_0$. When a CC calculation is performed subject to such a reference function, it too has the property that $\langle\Phi_0|\hat{S}^2 e^T|\Phi_0\rangle = S(S+1)$. Such a CC wavefunction is sometimes called projected [16]. Figure 1 shows a comparison of our results for C_4 using CCSD [A36] with the experimental spectra of Smalley, et al. [15]. The agreement is excellent, with the onset of the ionization at an almost indistinct shoulder being predicted to fall at 3.62 eV compared to the experimental value of 3.70 eV. The agreement with the next four ionizations appear to also be in excellent agreement. The distinction between the QRHF/CC results and the Koopman's theorem (SCF orbital energy) results demonstrates the inability of the latter to provide any reliable predictions. The difference of over an eV in

the first ionization clearly shows that the experimental photoionization spectra corresponds to that for linear C_4^-, not cyclic C_4^-.

E. The Coulomb explosion experiment is a clever new approach to determining the structure of transient species [17]. In essence, a source of cluster ions may be generated by laser sputtering from a graphite surface. Then the ions are accelerated. A photodetachment laser ionizes the electrons of anions selectively. Depending upon the energy required for the different structures, one can select cyclic C_4 instead of linear C_4. Using our computed values of 2.13 eV for the rhombus and 3.62 eV for the linear form, Algranati, et al were able to selectively generate the neutral, rhombic C_4 transient [17]. Upon impinging on a formvar foil, all the valence electrons are rapidly removed from the structure causing the molecule to "explode" due to the residual Coulomb repulsions among the positively charged nuclei. By following the path of the atoms, one can reconstruct the structure of the molecule just prior to its explosion. Since the pattern for rhombic C_4 is quite different from that for linear C_4, these authors concluded that they were seeing the rhombic form, previously predicted by theory [4,A16,12], for the first time.

F. The next important source of information about carbon clusters is their electronic excitation energies. Many unresolved questions remain, that besides being important to cluster science, are critical to assessing whether certain of the diffuse lines in the interstellar spectrum arise from carbon chains [18]. As previously discussed for C_4, it is possible to obtain some excited state information from single reference CC/MBPT calculations provided the states are of different electronic symmetry. However, for excited states of the same symmetry this is not possible. Furthermore, unlike ground states, excited states frequently have large weights for several important configurations. This tends to require a multi-reference approach to correctly describe such excited states. We have recently applied our Fock space MRCC methods to C_n, for n = 2 to 5. Excellent results are obtained as illustrated by those for C_3 shown in Tables 1–3. In particular, we predicted the $^3\Pi_g$ state to be located at 2.81 eV. It was found after this prediction by Bernath at 2.90 eV.

Our results on C_n clusters through 1991 are summarized in [A47].


$^1\Delta_g, ^1\Sigma_g^+$ $^1\Pi_g, ^1\Pi_u, ^1\Sigma_u^+$
$^3\Pi_g$ $^3\Pi_u$ $^3\Sigma_u^+$
$^3\Sigma_g^-$
$^3\Sigma_u^-$
0.0
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4.0
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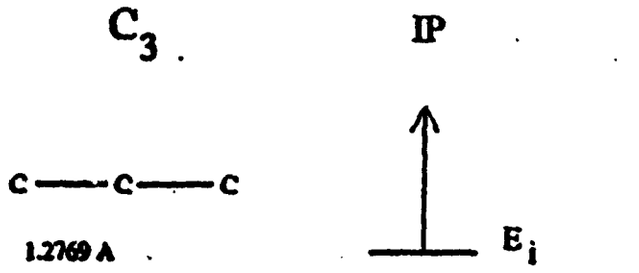
7.0
BINDING ENERGY (eV)

Fig. 1

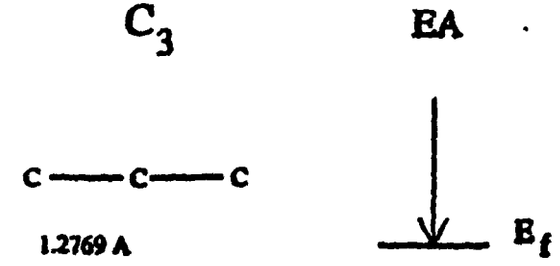
Table 1. Vertical ionization potentials (eV).



Electronic state	MC-SCF MR CI[3]	FSMRCC Basis I	FSMRCC Basis II	Exp. 1[3]	Exp. 2[3]
$^2\Sigma_u^+$	11.48 /11.46	11.80	11.97	12.1	11.1
$^2\Sigma_g^+$	12.21 /12.22	12.58	12.75		
$^2\Pi_u$	12.32 /13.11	13.36	13.48		

Basis I: [9s5p2d/4s2p1d] +1s1p (on bond) (56 fncns).
Basis II: [9s5p2d/5s3p2d] +1s1p (on bond) (86 fncns).
(1) Sunil, K.K., Orendt A. and Jordan K.D., Chem. Phys. 89, 245 (1984) [10s5p2d/3s3p1d] (54 fncns).
(2) Kohl, F.J. and Stevens C.A., J. Chem. Phys. 52, 6310 (1970).
(3) Gupta, S.K. and Gingerich, K.A., J. Chem. Phys. 71, 3072 (1979).

Table 2. Vertical electron affinities (eV).

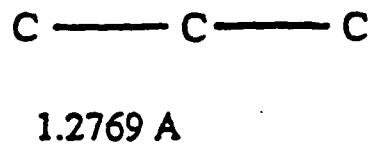


Electronic state	MC-SCF MR CI[1]	FSMRCC Basis I	FSMRCC Basis II	Experiment[2]
$^2\Pi_g$	1.07 /1.68	1.52	1.76	2.05

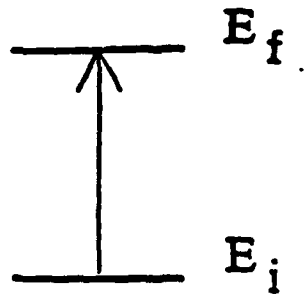
Basis I: [9s5p2d/4s2p1d] + 1s1p (on bond) (56 fncns).
Basis II: [9s5p2d/5s3p2d] + 1s1p (on bond) (86 fncns).
(1)(1) Sunil, K.K., Orendt A. and Jordan K.D., Chem. Phys. 89, 245 (1984) [10s5p2d/3s3p1d] (54 fncns).
(2)Oakes, J. and Ellison, G.B. as cited in ref. 19 in Sunil et al.

Table 3. Vertical excitation energies (eV).

C_3 EE



1.2769 A



Electronic state	MRD-CI Basis III /BasisII(*)	FSMRCC Basis I	FSMRCC Basis II	Experiment
$^3\Pi_u$	2.11	2.09	2.07	2.10
$^3\Pi_g$	2.82-2.92	2.82	2.81	2.90 **
$^3\Sigma_u^+$	3.36	3.25	3.16	
$^1\Pi_u$	3.16/3.258	3.29	3.23	3.06
$^3\Delta_u$	3.81	3.71	3.63	
$^1\Sigma_u^-$	4.10	4.06	4.00	Complicated band system ~4.1-4.7 eV.
$^3\Sigma_u^-$	3.99-4.08	4.06	4.01	
$^1\Delta_u$	4.13	4.12	4.08	
$^1\Pi_g$	4.17/4.096	4.26	4.19	
$^1\Sigma_u^+$	8.14	8.03	7.76	6.6

Basis I: [9s5p2d/4s2p1d] + 1s1p (on bond) (56 fncns).
Basis II: [9s5p2d/5s3p1d] + 1s1p (on bond) (86 fncns).
Basis III: DZ + 1s1p (on central atom) (42 fncns).
(*) Römelt, J., Peyerimhoff, S.D. and Buenker, R.J., Chem. Phys. Lett. 58, 1 (1978) / Chabalowski C.F. and Peyerimhoff, S.D., J. Chem. Phys. 84, 268 (1986).
** H. Sasada, T. Amano, C. Jarman, and P.F. Bernath, J. Chem. Phys. 94, 2401 (19

III. Other Clusters

A. Related to our work on carbon clusters, we have also studied the mixed $(SiC)_2$ clusters [A33]. Like the rhombic form of C_4, the lowest energy form of $(SiC)_2$ is also a rhombus, but it is much more stable compared to potential linear configurations. Analytic second derivative MBPT(2) methods [2] were employed to predict the vibrational spectra of these experimentally unknown but stable clusters in hopes that they will be observed.

B. Other cluster applications have been made to Be_3 [A31]. We assessed the importance of triple and quadruple excitation connected cluster operators in Be_3. Part of the objective was to identify a feasible but high level treatment of electron correlation sufficient to accurately describe large Be_n clusters. However, Be is notorious for the near degeneracy of its 2s and 2p orbitals, causing Be_2 to have unusual correlation effects leading to an unexpected minimum energy configuration at an R of about 5 a.u., instead of being the Van der Waal's molecule that Hartree-Fock MO theory predicts. This small but qualitatively important effect can only be described by the most sophisticated correlation methods like CCSDT. We wondered if similar complications could occur in Be_3. Hence we studied several iterative and non-iterative CC methods compared to full CI to assess their suitability. We found that the CCSD + TQ*(CCSD) method we introduced [19], which means add a non-iterative evaluation of triple and quadruple connected cluster operators after performing a CCSD calculation, worked quite well, while some of the simpler methods we invented like CCSD + T*(CCSD) [19] were still adequate for Be_n clusters.

C. We also studied hydrogen-bonded clusters such as that composed of HF and HO-NH_2 [A40]. We predicted the vibrational spectra of this cyclic form observing good agreement with that observed by Andrews, et al. [20].

D. We also present an extremely thorough study of the prototypical H-bonded system, $(H_2O)_2$ [A7]. The purpose was to assess, definitely, the superposition error in weakly bound hydrogen bonded complexes.

Methodological Advances

I. Fock space Multi-Reference Coupled-Cluster Theory

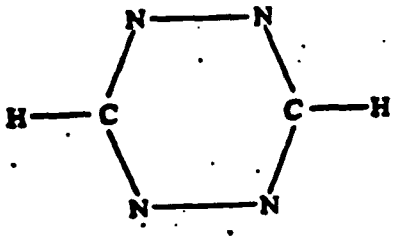
A. One of the primary new and powerful techniques that has been developed in this program is the multi-reference Fock space coupled-cluster (CC) theory [A5,A9,A12]. Single reference CC theory is now recognized as being probably the most accurate, easily applied high level correlated method in electronic structure theory. However, for some examples, the single reference starting point is inadequate. This is particularly true for excited electronic states when several, usually singly excited configurations are heavily weighted in the description of the excited state, and for some ionized or electron attached states, as are required to predict the photoelectron spectroscopic properties of clusters. Such problems require a multi-reference starting point. The Fock space technique is quite novel in electronic structure theory. The term Fock space emphasizes the use of a "universal" wave operator Ω, that has the property that $\psi_i = \Omega\psi_i^0$ where ψ_i is the exact solution and ψ_i^0 is a model function, $\psi_i^0 = \sum_\mu \phi_\mu c_{\mu_i}$, represented by the set of configurations $\{\phi_\mu\}$ that span a reference space.

What is fundamentally different about this method is that the same, universal wave-operator Ω applies for the N electron ground state, all N-1 ionized states, all N+1 electron attached states, and all N electron excited states. Furthermore, it is necessary to hierarchically solve the N electron ground state, then the N-1 electron problem (0,1), then the N+1 electron (1,0) problem, up to the N electron or (1,1) sector problem for excited states. Since all prior electronic structure methods invariably work in Hilbert space (i.e. a space with a fixed number of electrons), Fock space techniques are fundamentally new in the field. In our work for ONR besides developing the theory we also wrote very general purpose programs to apply this technique at the coupled-cluster single and double excitation (CCSD) level. The initial applications were made to the prototype systems H_2CO [19], N_2 and CO [A5]. Later we studied the difficult examples ketene $H_2C{=}C{=}O$ and diazomethane $H_2C{=}N{=}N$ [A12], all with excellent accuracy.

B. As ionization potentials are also obtained from Fock space MRCC techniques, we have devoted several studies to this problem. An initial application was to the ionization potentials of CH_2NH and CH_2PH, the latter experimentally unknown prior to our predictions[A18]. For CH_2NH we obtained exceptional agreement with experiment, and we observed good convergence with basis sets. For CH_2PH, following our calculations, experimental values were obtained and found to be in excellent agreement.

C. Although MRCCSD is an excellent level for many applications to ionizations, excited states and electron affinities, the question of the importance of the correlation effect due to triple excitations is important. We introduced this contribution by defining a non-iterative triples correction MRCCSD + T(MRCCSD) where a single evaluation of the dominant low-order triple excitation terms using converged MRCCSD amplitudes was made [A22]. Excellent results were obtained for several examples including N_2, H_2CO and CH_2.

D. General purpose computer programs were developed for the Fock space MRCCSD method and large scale applications have now been made for sym-tetrazine [A39]



the very difficult ozone molecule, O_3 [A45],and for carbon clusters C_2, C_3, C_4, and C_5 [A47]. These will be published shortly. The latter has been discussed briefly in the Cluster Studies summary.

II. Hilbert Space Multi-Reference Coupled-Cluster Theory

A. The Fock space, valence universal approach is particularly useful for describing the relative energies among ionized, excited and electron attached states. However, the reference state, itself, known as the (0,0) sector in Fock space, and from which the other ionized (0,1) sector, electron attached (1,0) sector, and excited (1,1) sector are determined; must be described with a single determinant reference. This prohibits including other important configurations

into the reference state, itself. However, for many problems like in bond-breaking, for open-shell singlet molecules, and for complicated open-shell situations where more than one determinant must be used in a correct zeroth-order description, a superior approach is offered by the Hilbert space or fixed-N, multi-reference CC methods. In the last couple of years of this project, we developed the theory and made the initial applications of this method [A27–A29,A41–A44].

B. The first application addressed the potential energy curves for the Li_2 molecule [A43]. These are shown in Fig. 2. The reference space consists of the configuration, $|1\sigma_g^2 1\sigma_u^2 2\sigma_g^2|$ and $|1\sigma_g^2 1\sigma_u^2 2\sigma_g^2|$, which fails to separate correctly, the several curves are seen to go smoothly to their respective separated atom limits. Agreement with full CI (i.e. the exact solution in the basis set) is within a few mhartrees throughout the curves.

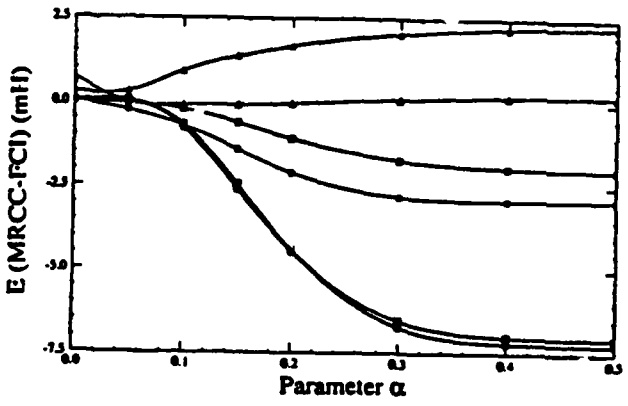


Fig. 2. Differences of minimal basis set MRCCSD correlation energies from exact FCI values ΔE, $\Delta E = E - E_{FCI}$, for the ground and three excited states of the model system H_4 (all deviations in mH) as a function of α (see text). The methods are identified as follows: fully-quadratic MRCCSD; (■) root X^1A_1; (□) root $^1A_1$; (▲) root $^3B_1$; (△) root $^1B_1$; MRCCSD including only the $\hat{T}_2^2/2$ quadratic contribution [35]; (●) root X^1A_1; (○) root $^1A_1$

C. The second application of this method considered the model problem of H_4 [41], where the geometry can be adjusted to reflect different degrees of degeneracy, with the maximum occurring at the square configuration. For such a degeneracy two configurations are critical in the description of the problem. Figure 3 shows the behavior of the calculations compared to full CI for a range of α which measures the degree of degeneracy. When α=0, the square configuration occurs with its maximum degeneracy. As is seen, the agreement between MRCC and full CI is exceptional.

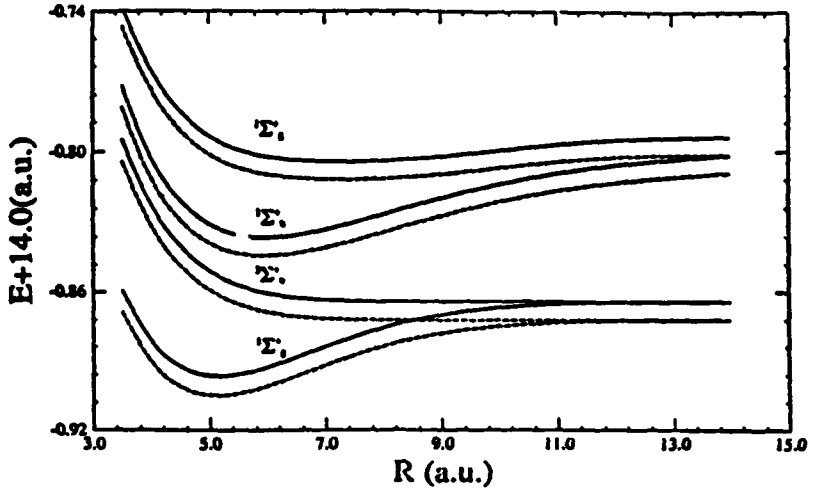


Fig.2. The multi-reference CCSD energies (in au) for the ground and three low-lying excited states of the Li_2 molecule. Being identical on this scale with the corresponding MRCC results, the FCI curves are not depicted. The curves are identified as follows: solid lines denote DZ values, and dashed lines the DZP values.

D. Any MRCC method can suffer from "intruder states." This occurs because an effective Hamiltonian, $H^{eff} = \langle\varphi|H\Omega|\varphi\rangle$ where $\{\varphi\}$ are the reference determinants and Ω the multi-reference CC waveoperator, must be diagonalized via $H^{eff}C = CE$ to obtain the several solutions. When the states are not close in energy (quasi degenerate), contributions from configurations outside the reference space can lead to energies that fall among the E obtained. This can cause singularities in H^{eff} making it impossible to extract the solutions for *any of the states*. A partial solution to the intruder state problem is to use an "incomplete" active space (IAS). The prior Li_2 and H_4 calculations used a "complete" active space (CAS) which means that for all orbitals considered active, *all* possible excitations among those that are allowed by symmetry are included. For Li_2, e.g., $2\sigma_g$ and $2\sigma_u$ are active, and since $|1\sigma_g^2 1\sigma_u^2 2\sigma_g^1 2\sigma_u^1|$ is of different symmetry, the two-configuration example above is complete. For LiH, instead, we have the four determinants $|1\sigma^2 2\sigma^2|$, $|\sigma^2 2\sigma\alpha^1 3\sigma\beta^1|$, $|1\sigma^2 2\sigma\beta^1 3\sigma\alpha^1|$ and $|1\sigma^2 3\sigma^2|$ for 2σ and 3σ active. If all four are used, the singly occupied determinants lead to an intruder state for this example. Consequently, we formulated an IAS MRCC method [A27,A28] and proved a linked diagram theorem that applied even for the IAS, which had previously not been thought to be possible. This first application of IAS-MRCC was presented for excited states of LiH [A42].

E. The *bête noire* of single-reference CC methods occurs for open-shell singlet states, like $\frac{1}{\sqrt{2}}[|\text{core}1a_1\alpha^1 1b_2\beta^1| - |\text{core}1a_1\beta^1 1b_2\alpha^1|]$ For such a case, two determinants are exactly equally weighted in the zeroth-order description of the open-shell singlet. There is no justification whatsoever, for designating one of the two determinants as the "reference" and relegating the other to the complementary (Q) space to be introduced perturbatively. Hence, a proper description demands the multi-reference starting point. We solved this previously intractable problem in CC theory by using the Hilbert space MRCCSD approach. The initial applications to excited states (the latter occurs when the minus sign is replaced by a plus sign) for O_3 are shown in Table 4 [A46]. We also report results for other examples like ketene and diazomethane where both open-shell orbitals are of the same symmetry, (i.e. a_1 and b_2) which leads to an IAS open shell singlet [A46].

Table 4. Vertical excitation energies for ozone, ketene, and diazomethane. (eV).

State	Multi-reference CCSD		Single-reference CCSD		Exp.
	Fock space[a]	Hilbert space[b]	QRHF[c]	UHF	
Ozone: r_{O-O}=1.263Å, <OOO=117.4°, E=-224.908 358 a.u.[d]					
$^3B_2$	1.37	1.38	1.21	1.16	
$^1B_2$	5.52	5.71			4.9
$^3B_1$	1.62	1.66	1.63	1.56	
$^1B_1$	2.13	2.26			2.1
$^3A_2$	1.96	1.89	1.87	1.80	
$^1A_2$	2.17	2.24			1.6
Ketene: r_{C-O}=1.161Å, r_{C-H}=1.083A, r_{C-C}=1.314A, <HCH=122°35', E=-152.206 938 a.u.[d]					
$^3A_2$	3.78	3.75	3.75	3.73	3.34
$^1A_2$	3.83	3.83			3.84
$^3A_1$	5.43	5.81	5.67	5.65	5.33
$2\ ^1A_1$	7.89	8.64			6.78
$2\ ^3A_1$	7.12	7.84	7.58		
$3\ ^1A_1$	10.42	10.26			
Diazomethane: r_{C-N}=1.320Å, r_{C-H}=1.080Å, r_{N-N}=1.120Å, <HCH=127°, E=-148.344 853 a.u.[d]					
$^3A_2$	2.92	2.81	2.81	2.79	
$^1A_2$	3.24	3.05			3.14
$^3A_1$	3.97	4.08	3.95	3.93	
$2\ ^1A_1$	6.24	6.75			5.70
$2\ ^3A_1$	7.02	7.39	7.27		
$3\ ^1A_1$	10.36	9.82			

[a]Fock space MRCC excitation energies for ozone, ketene and diazomethane
[b]Present results.
[c]QRHF-CCSD results are obtained from the ground state (N-electron singlet) reference.
[d]The geometry and CCSD reference energy for the ground state. In post-SCF calculations the 1s orbitals were kept frozen and the highest three virtual orbitals were not allowed to contribute to the correlated calculations.

III. Optimum Virtual Orbital Space

F In a different vein, the problem of basis sets in electronic structure theory is also critical. Since correlated methods scale as n^6 to n^8 for n basis functions in the most popular CC/MBPT and CI methods, it is clear that even doubling the size of basis set can lead to a factor of two to four orders of magnitude in computer time required for a calculation. To help alleviate this problem, we introduced our optimized virtual orbital space (OVOS) method [22,A4]. This effectively reduces the dimension of a basis set at comparatively little cost in accuracy. The basic idea is to exploit the Hylleraas variational principal for the second order (MBPT(2)) correlation energy correction to define an *optimum* transformation of the large, n_v set of virtual orbitals to m_v contributions where $m_v << n_v$. Since this transformation gives the lowest possible second-order energy, the resulting smaller set of excited correlating orbitals are particularly well chosen to describe the higher order correlation via CCSD, CCSDT, and other methods. Our initial papers [21,A4] considered potential energy surfaces for HOOH, B_2H_6, CH_2 and other examples involving electric field properties. The conclusions are that with even one-half as many optimum orbitals, we can save more than two orders of magnitude in the calculation time and obtain close to 99% of the correlation energy in the basis set. We also applied this technique to the question of the comparative stability of three tautomers of the nucleic acid base cytosine [A19]. This very large correlated calculation indicates the power of the method.

IV. Other Methodological Studies

G Several papers [A11, A25, A26] dealt with the behavior of a variety of single reference CC theories for the harmonic frequencies and dissociation energy of O_3, a well-known multi-reference problem. It was shown that CCSD + T(CCSD) failed and that CCSDT-1 works less well than usual. However, CCSDT-2 did very well in resolving the inherent multi-reference character possessed by O_3.

H Another quite important methodological development during the course of this project has been the general relaxed density theory for analytical first and second derivatives for CC/MBPT methods [A14,A15]. The first implementation was made for MBPT(3) [1] and has now been extended to higher levels. Only with the existence of such analytical gradient tools is it reasonable to obtain the molecular structure of polyatomic clusters with electron correlation.

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1. S. Kucharski and R.J. Bartlett, "Multi-Reference Many-Body Perturbation Theory," Int. J. Quantum Chem. Symp. **22**, 383 (1988).
2. L. Adamowicz, R.J. Bartlett and A.J. Sadlej, "Optimized Virtual Orbital Space for High-Level Correlated Calculations II. Electric Properties," J. Chem. Phys. **88**, 5749 (1988).
3. J.F. Stanton, W.N. Lipscomb and R.J. Bartlett, "Structure, Energetics and Vibrational Spectra of Beryllium Borohydride Isomers," J. Chem. Phys. **88**, 5726 (1988).
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47. M. Rittby and R.J. Bartlett, "Electronic Excitation Spectra of Carbon Clusters," to be published.

Honors/Awards/Prizes

1. Promotion to Graduate Research Professor of Chemistry and Physics, 1988 (a rank attained by only 2% of faculty)
2. Elected a fellow of the International Academy of Quantum Molecular Sciences, Menton, France, 1991. Only 30 members younger than 65 are allowed, and 65 members total.
3. Fellow, American Physical Society, 1989
4. Editorial Board, Journal of Chemical Physics, 1990–present
5. Advisory Board, Theoretical Chimica Acta, 1987–present
6. Editorial Board, International Journal of Quantum Chemistry, 1985–1989

7. Editorial Board, Molecular Physics, 1992–

Invited Presentations Supported by ONR 1988–1991

August, 1991 — Fourth Chemical Congress of North America, New York City, NY
June, 1991 — Workshop on Recent Developments in Electronic Structure Algorithms, Ithaca, NY
May, 1991 — American Chemical Society Joint Central-Great Lakes Regional Meeting, Indianapolis, IN
August, 1990 — Workshop on Coupled-Cluster Theory at the Interface of Atomic Physics and Quantum Chemistry, Cambridge, MA
July, 1990 — Seventh American Conference on Theoretical Chemistry, San Diego, CA
July, 1990 — Seventy-Third Canadian Chemical Conference, Halifax, NS
June, 1990 — W.N. Lipscomb 70th Birthday Symposium, Cambridge, MA
January, 1990 — ONR Clusters Program Meeting, Lake Arrowhead, CA
October, 1989 — Meeting on Forty Years of Quantum Chemistry, Athens, GA.
October, 1988 — Symposium on Quantum Chemistry, High Tatras, Czechoslovakia.
September, 1988 — 2nd International Symposium - Computational Chemistry on Cray Supercomputers, Chicago, IL.
August, 1988 — Many-Body Methods in Quantum Chemistry, Satellite Symposium to the Sixth International Congress on Quantum Chemistry, Tel Aviv, Israel.
August, 1988 — Sixth International Congress on Quantum Chemistry, Jerusalem, Israel.
June, 1988 — Workshop on Quantum Chemistry, Basic Aspects, Actual Trends, Girona, Spain.
February, 1988 — Workshop and Symposium on Aspects of Many-Body Effects in Molecules and Extended Systems, Calcutta, India.

Students Partially Supported by ONR 1988–1991

1. Tadeusz Pluta — Ph.D. 1990
2. Reneé Peloquin Mattie, 1988–present
3. David Bernholdt, 1988–present
4. Sullivan Beck, 1991–present
5. S. Ajith Perera, 1991–present

Postdoctoral Associates Partially Supported by ONR 1988–1991

1. Dr. John Watts, 1988–present
2. Dr. John Stanton, 1989–1990
3. Dr. Anna Balkova, 1989–present
4. Dr. Leszek Meissner, 1989–91
5. Dr. Stanislaw Kucharski, 1989–1991